

Exposure to Particulate Matter, Volatile Organic Compounds, and Other Air Pollutants Inside Patrol Cars

MICHAEL RIEDIKER,[†]
RONALD WILLIAMS,[‡] ROBERT DEVLIN,[§]
THOMAS GRIGGS,^{||,⊥} AND
PHILIP BROMBERG[†]

*Center for Environmental Medicine,
Asthma and Lung Biology, School of Medicine,
University of North Carolina at Chapel Hill, North Carolina,
U.S. EPA, ORD, National Exposure Research Laboratories,
RTP, North Carolina, U.S. EPA, ORD, National Health and
Environmental Effects Research Laboratories, RTP,
North Carolina, North Carolina State Highway Patrol, and
Division of Cardiology, School of Medicine, University of
North Carolina at Chapel Hill, North Carolina*

People driving in a vehicle might receive an enhanced dose of mobile source pollutants that are considered a potential risk for cardiovascular diseases. The exposure to components of air pollution in highway patrol vehicles, at an ambient, and a roadside location was determined during 25 work shifts (3 p.m. to midnight) in the autumn of 2001, each day with two cars. A global positioning system and a diary provided location and activity information. Average pollutant levels inside the cars were low compared to ambient air quality standards: carbon monoxide 2.7 ppm, nitrogen dioxide 41.7 $\mu\text{g}/\text{m}^3$, ozone 11.7 ppb, particulate matter smaller 2.5 μm ($\text{PM}_{2.5}$) 24 $\mu\text{g}/\text{m}^3$. Volatile organic compounds inside the cars were in the ppb-range and showed the fingerprint of gasoline. $\text{PM}_{2.5}$ was 24% lower than ambient and roadside levels, probably due to depositions associated with the recirculating air conditioning. Levels of carbon monoxide, aldehydes, hydrocarbons, and some metals (Al, Ca, Ti, V, Cr, Mn, Fe, Cu, and Sr) were highest in the cars, and roadside levels were higher than ambient levels. Elevated pollutant levels were related to locations with high traffic volumes. Our results point to combustion engine emissions from other vehicles as important sources of air pollutants inside the car.

Introduction

Vehicles represent a microenvironment with potentially high concentrations of toxic air pollutants. Exposure to these pollutants can be important to the general population since

the American population spends on average 6.6% of its time (95 min each day) inside vehicles (1). Previous studies showed an association between ambient airborne particulate matter (PM) exposure and death and hospitalization due to heart attacks, strokes, and other cardiovascular events (2–4). Some studies (5, 6) proposed that exposure to PM and other pollutants from motor vehicles and other mobile sources might be especially harmful. For professionals such as truck, bus, and taxi drivers or motorized police officers, this exposure might pose an occupational hazard.

Computer models suggest that even a small amount of time spent in vehicles may contribute significantly to the average daily personal exposure to PM and gaseous pollutants (7, 8). The results of these models were confirmed in studies where subjects recorded their normal activity in parallel with personal exposure measurements for PM_{10} (particles with aerodynamic diameter $< 10 \mu\text{m}$) and carbon monoxide (CO) but remained inconclusive for $\text{PM}_{2.5}$ ($< 2.5 \mu\text{m}$) (8, 9).

Commuters are exposed to higher than average levels of air pollutants. This has been shown for a wide variety of vehicles, such as cars, buses, subways, and bicycles. Particulate matter levels within vehicles are usually well above ambient levels as reviewed by Adams et al. (10). Their study conducted in London reported the $\text{PM}_{2.5}$ exposure in transport microenvironments during commutes to be on average 2-fold the urban background concentration for all the types of commuting styles investigated. CO levels inside cars during commutes have been reported to be several ppm above ambient levels (11–13) despite a decreasing trend for in-vehicle CO levels over the past four decades (14). Volatile organic compounds (VOCs) have also been reported to be elevated inside vehicles during commutes (15–17). These studies focused on commuting and provide valuable information for understanding the exposure of the general population to toxic air pollutants.

Truck, bus, and taxi drivers spend most of their working time in vehicles. A survey by the American trucking industry in the late 1980s (18) showed elevated personal exposures to diesel exhaust particles for truck drivers compared to residential background concentrations. Inside French public buses, levels of CO, NO_x , lead, and aldehydes were also elevated and similar to levels measured in front of the bus (19). Studies of taxi drivers in Paris, France (20), London, England (21), and Taegu, South Korea (22) reported elevated levels for CO, NO_x , VOCs, and metals compared to ambient levels. Interestingly, the average VOC exposure for taxi drivers in Taegu was similar to the average concentrations reported earlier for commutes in the same city (23). This suggests that driving in an urban area is by itself an important factor for the VOC exposure.

In this study, we investigated a wide range of real-time and integrated PM and gaseous pollutants in order to better understand the potential occupational exposure of North Carolina State Highway Patrol Troopers to toxic air pollutants during their regular work. We included a global positioning system (GPS) device inside the vehicle to link the collected data with time-space coordinates. In addition, a number of health endpoints were assessed in the participating troopers such as lung function, ambulatory electrocardiogram, and blood parameters. In this paper we describe the exposures inside the patrol cars.

Methods

Study Design. Ten nonsmoking North Carolina State Highway Patrol (NCSHP) troopers were monitored during a total of 25 days in August, September, and October 2001. Two

* Corresponding author phone: ++41-1-632 0884; fax: ++41-1-632 1173; e-mail: Michael.Riediker@alumni.ethz.ch. Corresponding author address: IHA, NW F77, ETH Zentrum, 8092 Zürich, Switzerland.

[†] Center for Environmental Medicine, Asthma and Lung Biology, School of Medicine, University of North Carolina at Chapel Hill.

[‡] National Exposure Research Laboratories, RTP.

[§] National Health and Environmental Effects Research Laboratories, RTP.

^{||} North Carolina State Highway Patrol.

[⊥] Division of Cardiology, School of Medicine, University of North Carolina at Chapel Hill.

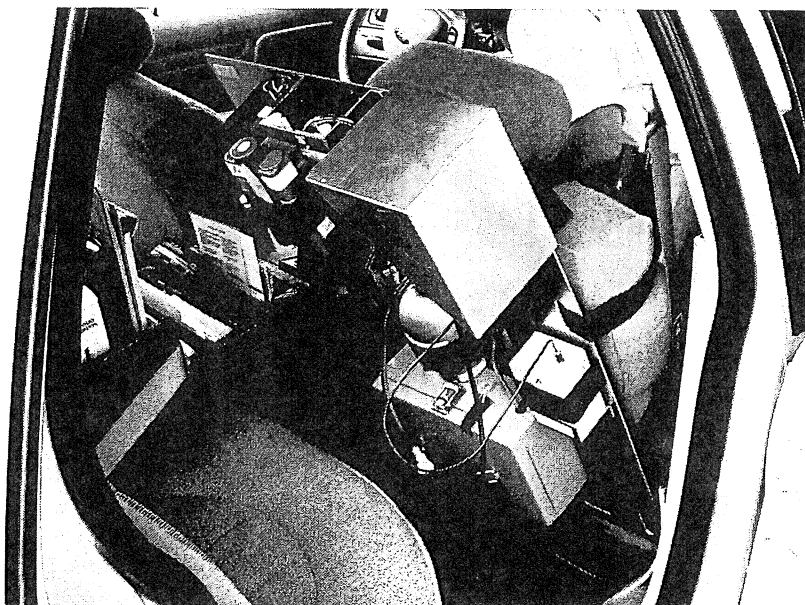


FIGURE 1. The aluminum boards were securely strapped to the back of the front passenger seat. The monitors are on the top of the board, pumps and batteries at the bottom. An aluminum shield protected the monitors near the window from direct sun exposure.

troopers were monitored each day, resulting in a total of 50 examined shifts. Each trooper was monitored in his personal patrol car on four consecutive workdays (Monday thru Thursday) while on his late shift, which lasted from 3 p.m. to midnight. During this shift the troopers spend the least amount of time away from their car. The troopers' assigned work area was Wake County, the area in and around Raleigh, the capital of North Carolina. The NCSHP medical office in South Raleigh served as the starting point for all the monitoring. The current standard vehicle of the NCSHP is the 1998–2000 Ford Crown Victoria powered by a 4.6-L V8 gasoline engine with an efficiency of 13.1 L per 100 km (18 miles per gallon) (24). The cars have air conditioning and a fresh air intake without filtration. They are equipped with cloth seats.

Each patrol car was equipped with a number of portable air quality monitors. Continuously measured variables were temperature, relative humidity, particles with an aerodynamic diameter smaller $2.5\ \mu\text{m}$ (50% cut point, $\text{PM}_{2.5}$), carbon monoxide (CO), and polycyclic aromatic hydrocarbons (PAH). Integrative samplers were used to measure $\text{PM}_{2.5}$ mass, elemental carbon, elemental composition of $\text{PM}_{2.5}$, nitrogen dioxide (NO_2), ozone, aldehydes, and volatile organic compounds (VOCs). The route of the car was monitored with a GPS tracking device. The troopers recorded in a time-activity diary the settings of the ventilation system and getting in and out of their car. Excerpts of the official log specifying times and types of law enforcement activities were also made available to us.

For comparison purposes, the same exposure variables measured in the patrol cars were measured simultaneously at one fixed ambient station and at a changing roadside location. The ambient site was located in northern Raleigh, colocated with the Millbrook monitoring site of the North Carolina Department of Environment and Natural Resources (NCDENR). The roadside monitors were located in Wake County near major traffic routes. They remained for four consecutive days at each roadside location.

Technical Details. The Institutional Review Board of the UNC School of Medicine approved the study. Written consent was obtained from all troopers before their participation in the study. All instruments were mounted in our laboratory on an aluminum board and transported to the NCSHP medical office, where the boards were securely strapped on

the backside of the front passenger seat (Figure 1). The instruments were started at the beginning of the work shift and were operated until the end of the shift. After each shift, the boards were returned to the laboratory for sample recovery, data downloading, and to prepare the monitors for the next shift.

Below follows a description of the instruments and methods used. For electronic devices, estimates for limit of detection, precision, and accuracy are according to manufacturer's description. Estimates for laboratory procedures are based on experience values and quality control results. Quality control for all integrative samplers included duplicate and blank sampling on 10% of the sample days as well as duplicate laboratory analyses.

Temperature and relative humidity data were measured with HOBO sensors (Onset Computer Corp., Pocasset, MA) in 1-minute intervals. Instrument precision and accuracy are both $\pm 1\ ^\circ\text{C}$ and $\pm 5\% \text{ rH}$.

CO was measured in 30-s intervals using a portable Langan T15 CO gas monitor (Langan Products Inc., San Francisco, CA), which measures CO concentrations with an electrochemical sensor. The CO monitors were calibrated daily (zero air and 10 ppm CO span). The downloaded data were subsequently span- and temperature-corrected based on the daily span and monitor-specific temperature profiles. Precision and accuracy were both $\pm 20\%$.

PAHs on fine particles were measured as 20 s averages using a photoionization detector, PAS 2000CE (EcoChem Analytics, League City, TX). The monitors were cross-corrected based on colocated in-vehicle measurements conducted before and after the study. The monitors were manufacturer calibrated for PAH on urban aerosols. The results correspond approximately to the amount of PAH bound on particles sized around $1\ \mu\text{m}$ aerodynamic diameter (25). The limit of detection (LOD) was $10\ \text{ng PAH/m}^3$. Precision and accuracy are estimated to $\pm 10\%$. These measurements were conducted inside the cars only.

The speed, direction and location of the car were determined every 30 s with a 12-channel Global Positioning System GPS III Plus (Garmin Intl. Inc., Olathe, KS). A magnetic roof antenna was used to improve the quality of the signal reception. The precision was $\pm 5\ \text{m}$, the accuracy ± 15 to $100\ \text{m}$.

Approximate realtime PM_{2.5} concentrations (PM_{2.5Realtime}) (~0.3–2 µm) were measured as 1-minute averages with nephelometers (personalDataRam, MIE, Inc., Bedford, MA). The nephelometers were zeroed daily in the lab before the work shift. They were manufacturer calibrated to an aerosol of PM_{2.5} road dust. In previous studies, the sampler was found to be influenced by high levels of relative humidity (26). Therefore values of PM_{2.5Realtime} obtained during episodes of relative humidity above 85% were not used. The precision and accuracy were both ±20%.

PM_{2.5Mass} particles were collected with a PM_{2.5} PEM sampler (SKC, Eighty Four, PA) using a flow of 4 L per minute onto preweighed 37 mm Teflon filters (Teflo-Gelman Sciences, Ann Arbor, MI). The flow was measured at the inlet at the beginning and the end of the sampling period using a DryCal Lite flow meter (Bios Intl., Butler, NJ). Total mass PM_{2.5Mass} was determined gravimetrically by weighing the filters before and after sampling after conditioning for 24 h at room temperature and 50% relative humidity (±5%) (LOD: 2 µg/m³). Filters were analyzed for elemental carbon by an updated nondestructive light transmission methodology (27), with a LOD of 0.2 µg/m³. XRF (X-ray fluorescence) analysis of the same filter samples was conducted by Chester LabNet (Portland, OR) using EPA method IO-3.3, protocol 6, for the XRF analysis for 48 elements from Na to Pb (Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Ir, Au, Hg, Pb). The precision and accuracy were both ±5%. The filter samples were then stored for future analysis.

The ozone and NO₂ concentrations were determined using passive sample badges (Ogawa Inc., Pompano Beach, FL). They contain coated filters, which react with ozone or NO₂, respectively, to form an adsorbent product. The adsorbent was then extracted and analyzed using ion chromatography columns (Supelco, Bellefonte, PA) (28). The LOD was 10 ppb.

Aldehydes were collected with dinitrophenylhydrazine (DNPH)-coated silica gel cartridges using sampling pumps at a flow of approximately 0.2 L per minute. The flow was measured at the beginning and the end of the sampling with a DryCal Lite flow meter (Bios Intl., Butler, NJ). Potassium iodide scrubbers were used in front of the DNPH-cartridge to trap ozone. High Performance Liquid Chromatography with UV detection was used to detect and quantify the following aldehyde and carbonyl species: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, *n*-butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, *m*-tolualdehyde, *o*,*p*-tolualdehyde, hexanaldehyde, 2,5-dimethylbenzaldehyde, and acetone (29). The LOD was for each ca. 0.5 µg/m³.

Volatile organic carbon compounds (VOCs) were collected using 1-L Summa electropolished vacuum canisters (SIS Inc., Moscow, ID) evacuated before sampling to a pressure of 0.033 Pa or better. Each canister was fitted with a passive resistive flow element for sampling, prototypes of Veriflow flow controllers (Biospherics, Inc. Hillsboro, OR). The sampler flow rates were set using a digital electronic flow calibrator (#21606, Restek Corp., Bellefonte, PA). To achieve up to 10-h nominal integration time, the flow controllers were set for approximately 1.2 mL/min. Post-sampling pressure checks were performed on each canister to ensure validity of the samples. Canister preparation and subsequent analysis by gas chromatography were performed as described in (30). Quantitative analysis was performed for 1,3-butadiene, *n*-butane, *n*-pentane, butanal, *n*-hexane, benzene, *n*-heptane, toluene, hexanal, *n*-octane, ethylbenzene, *m*,*p*-xylene, heptanal, *o*-xylene, *n*-nonane, *p*-ethyltoluene, 1,3,5-trimethylbenzene, octanal, 1,2,4-trimethylbenzene, *n*-decane, nonanal, and *n*-undecane. The LOD for these pollutants was 1–6 ppb.

At the Millbrook air quality monitoring site in northern Raleigh, NC DENR measures PM_{2.5} with a tapered element oscillating microbalance (TEOM) – monitor and ozone with a chemiluminescence monitor. The data were kindly provided by NC DENR after they had been verified and submitted to quality control analysis.

Statistics were calculated using SYSTAT 10 for Windows (Richmond, CA). To compare the different locations the Whitney–Mann U-test was used. Paired data were compared using the Wilcoxon sign test. Most correlations were calculated using the Spearman rank test. The VOC data from the canisters at the different locations were analyzed with a hierarchical clustering procedure (average distance linkage of the Pearson-distances) and displayed in cluster trees. The impact of outliers on the results was examined by temporarily excluding them from the statistical calculations. Outliers that could clearly be attributed to laboratory or handling problems were excluded from the analysis.

Results

Patrol Routes and Activities. From August 13 to October 11, 2001, 50 late-shift patrols (3 p.m. to midnight) were successfully monitored. The equipment stayed safely in place on the back of the passenger seat during all the patrols, even when the cars were involved in chases. The average patrol lasted 9:06 h, ranging from 7:45 to 14:40 h. The troopers patrolled all areas of rural and urban Wake County, with the predominant area of service on and near major highways and interstates. During these patrols, the troopers worked on 68 accidents (11 with personal injuries), arrested 7 drivers (6 due to intoxication), responded to 39 other incidents, and issued 173 citations. On average, troopers spent 35% of their shift away from the car, either in the office, in jail, in hospitals, for dinner (up to 1 h per patrol), or on special assignments for the protection of sensitive locations (after September 11). On average, troopers drove 204 km per work shift (standard deviation 74 km, range 86–430 km). The GPS recordings allowed clear identification of the location, direction, and speed of the car and were helpful in better understanding the activities of the troopers. Battery failure prevented complete collection of GPS information during two shifts.

Climate and Key Pollutants in the Cars and at the Stationary Sites. Table 1 summarizes the daily data of climate, airborne particulates, NO₂, and ozone. The maximum concentration of NO₂ inside the vehicles (548.5 ppb) is an extreme outlier (over 6 SD larger than the mean). Levels of other pollutants were not elevated during that shift. The average NO₂ concentration inside the vehicles is 31.4 ppb if this extreme value is omitted. Blank values for ozone were higher than expected; the presented blank-corrected values might therefore underestimate the real value (see the negative minimum value).

The relative humidity at the roadsides and the ambient site was often above 85%. During episodes of high humidity, the real time PM_{2.5} monitor (MIE Personal DataRam) recorded exposure estimates reaching the milligram range. The subsequent omission of values from episodes with relative humidity above 85% resulted in a large proportion (32%) of PM_{2.5Realtime} data to be omitted. The remaining shift averages of PM_{2.5Realtime} were significantly correlated to PM_{2.5Mass} (Spearman test: ambient $r = 0.56$, roadside $r = 0.73$, in car $r = 0.74$) and the mean concentrations were not different (Wilcoxon test, all $p > 0.2$). There was no loss of data inside the vehicles, since relative humidity inside the vehicles was always below 85%.

The activity log of the troopers allowed comparing the continuously measured variables for times when the troopers were using their cars with times the cars were sitting unoccupied in parking lots with engines shut down (on average 35% of the patrol duration). The pollutant concen-

TABLE 1: Summary for the Daily Data of Climate, Airborne Particulates, NO₂, and Ozone^b

location	parameter units	duration, h	temp, °C	relative humidity, %	CO, ppm	PM _{2.5} Realtime, μg/m ³	PM _{2.5} Mass, μg/m ³	elemental carbon, μg/m ³	NO ₂ , ppb	ozone, ppb
patrol cars	mean	9:06	25.5	35.8	2.6	24.1	23.0	2.3	41.7	11.7
	SD	1:00	2.1	5.5	1.1	14.6	10.8	0.8	83.3	15.9
	minimum	7:45	20.3	25.7	0.7	4.4	6.8	1.1	1.6	-4.6
	maximum	14:40	30.4	46.0	5.9	54.4	58.7	5.0	548.5 ^a	69.9
ambient site	mean	8:17	24.3	62.9	0.8	35.4	31.7	1.7	30.4	28.3
	SD	0:23	4.9	13.7	0.3	25.3	13.8	0.7	17.1	15.8
	minimum	7:06	11.1	45.1	0.3	3.9	9.9	0.6	9.4	6.0
	maximum	9:04	30.1	95.4	1.5	96.0	68.9	3.7	69.5	61.4
roadside	mean	8:23	23.3	67.4	1.1	30.9	29.9	4.0	49.9	22.8
	SD	0:36	4.8	13.3	0.3	22.6	12.7	1.4	37.2	13.3
	minimum	6:50	11.1	45.3	0.4	5.8	8.9	1.1	13.0	3.5
	maximum	9:15	28.3	99.9	1.7	78.3	62.3	6.6	212.1	63.9
Millbrook (=ambient)	mean	9:00	23.0	71.3		22.2				31.2
	SD	0:00	4.5	11.2		9.8				13.8
	minimum	9:00	10.2	53.7		6.5				12.0
	maximum	9:00	28.7	97.1		38.8				55.3
<i>p</i> -values	car/ambient	0.094	0.808	0.000	0.000	0.114	0.006	0.001	0.241	0.000
	car/roadside	0.434	0.149	0.000	0.000	0.361	0.024	0.000	0.000	0.000
	ambient/road	0.397	0.314	0.119	0.013	0.503	0.782	0.000	0.006	0.103

^a The maximum NO₂ value inside the cars is an extreme outlier (average without this value is 31.4 ppb, SD 40.3 ppb). ^b Statistics: Mann–Whitney U-test.

TABLE 2: Average Concentrations of Aldehydes and Hydrocarbons Measured during the Study^a

parameter	units	patrol cars				ambient site				roadside			
		mean	SD	min	max	mean	SD	min	max	mean	SD	min	max
aldehydes (DNPH tubes)	μg/m ³	38.1	17.1	0.0	89.7	13.7	5.1	2.8	22.1	12.6	5.8	0.0	25.2
C4–C11 <i>n</i> -alkanes	ppb	33.2	54.9	5.1	335.8	4.3	3.1	1.6	13.3	3.9	2.1	1.1	10.8
benzene	ppb	4.0	3.2	0.4	13.5	0.1	0.2	0.0	0.6	0.2	0.3	0.0	0.8
toluene	ppb	10.4	20.2	2.3	130.8	1.7	0.9	0.8	4.7	1.5	0.7	0.6	3.3
xylenes	ppb	4.5	2.0	1.4	12.1	1.0	0.5	0.4	2.4	1.0	0.4	0.4	1.9
ethyl benzene	ppb	0.9	0.4	0.3	2.6	0.2	0.1	0.1	0.5	0.2	0.1	0.1	0.5
<i>p</i> -ethyl toluene	ppb	0.4	0.2	0.1	1.1	0.1	0.1	0.0	0.4	0.2	0.1	0.0	0.4
trimethyl benzenes	ppb	2.0	0.8	0.7	4.1	0.6	0.3	0.3	1.7	0.6	0.2	0.2	1.2

^a The patrol car data does not include four measurements from one car that had extreme values, which increased from shift to shift. Significances tested with the Mann–Whitney U-Test for all parameters: Patrol cars vs ambient or roadside $p < 0.0001$; ambient vs roadside not significant.

trations in the occupied cars were significantly higher compared to the parked cars (Mann–Whitney U-test). PM_{2.5}Realtime and CO were 30% higher (average PM_{2.5}Realtime in an occupied car: 26.7 μg/m³, in a parked car 20.8 μg/m³, $p = 0.04$, CO: 2.8 vs 2.2 ppm, $p = 0.02$), and the PAH-readings were doubled (26.0 vs 13.5 ng/m³, $p < 0.0001$). In contrast, the temperature and the relative humidity were 12% lower in the occupied cars ($p < 0.02$).

Comparison of Our Data with NCDENR Millbrook Data. Additional data for climate, PM_{2.5}, and ozone were obtained from the NCDENR fixed station “Millbrook” in northern Raleigh, which was colocated with our ambient site (summary data listed in Table 1). Climate variables did not differ significantly between the NCDENR fixed station and our colocated ambient site. The NCDENR fixed station PM_{2.5} measurements obtained with a TEOM particle meter was significantly (Wilcoxon, $p < 0.001$) lower than our ambient PM_{2.5}Realtime and PM_{2.5}Mass measurements. However, the correlations for PM_{2.5} were $r = 0.82$ between TEOM and PM_{2.5}Mass and $r = 0.63$ between TEOM and PM_{2.5}Realtime. Ozone data obtained with passive sampling badges were compared with the NCDENR data from the Millbrook site with a Pearson- r of 0.76 and the averages of the two methods were not different.

Concentrations of Aldehydes and VOCs. Aldehyde and VOC concentrations in the cars were significantly higher compared with those at roadside and ambient locations as summarized in Table 2. The table does not include four values from one car, which had strongly increasing hydrocarbon

values on all four patrols of that week (maximum of 5084 ppb total hydrocarbons). The average hydrocarbon concentrations would be about 2–4-fold higher with these values included. The aldehyde concentrations remained in an average range during these patrols (within 2 SD from the mean).

Not detectable throughout the study were isovaleraldehyde (< 0.5 μg/m³), *m*-tolualdehyde (< 0.5 μg/m³), and 1,3-butadiene (< 6.5 μg/m³). The concentrations of acrolein, *o*-*p*-tolualdehyde, and 2,5-dimethylbenzaldehyde were always small, with over 75% of the samples below the detection limit (< 0.5 μg/m³) and with a maximum acrolein concentration of 1 μg/m³. For all other substances, less than 25% of the samples were below the detection limit. The acetone data are not available due to contaminations of laboratory equipment with acetone.

For the VOCs sampled with canisters, we performed a cluster analysis (Figure 2). The patrol-car analysis shows that one strong cluster was formed by the shorter *n*-alkanes (C₄–C₉) and single ring aromatics. The aldehydes and longer *n*-alkanes were not tightly grouped. The clustering is weaker for the ambient and roadside measurements. The strongest subcluster included the chemically closely related xylenes and ethylbenzene.

Element Concentrations in the Collected PM_{2.5} Mass. The PM_{2.5} mass collected was analyzed by XRF for most elements from sodium (Na) to lead (Pb). Table 3 shows the average concentrations at the three different sampling

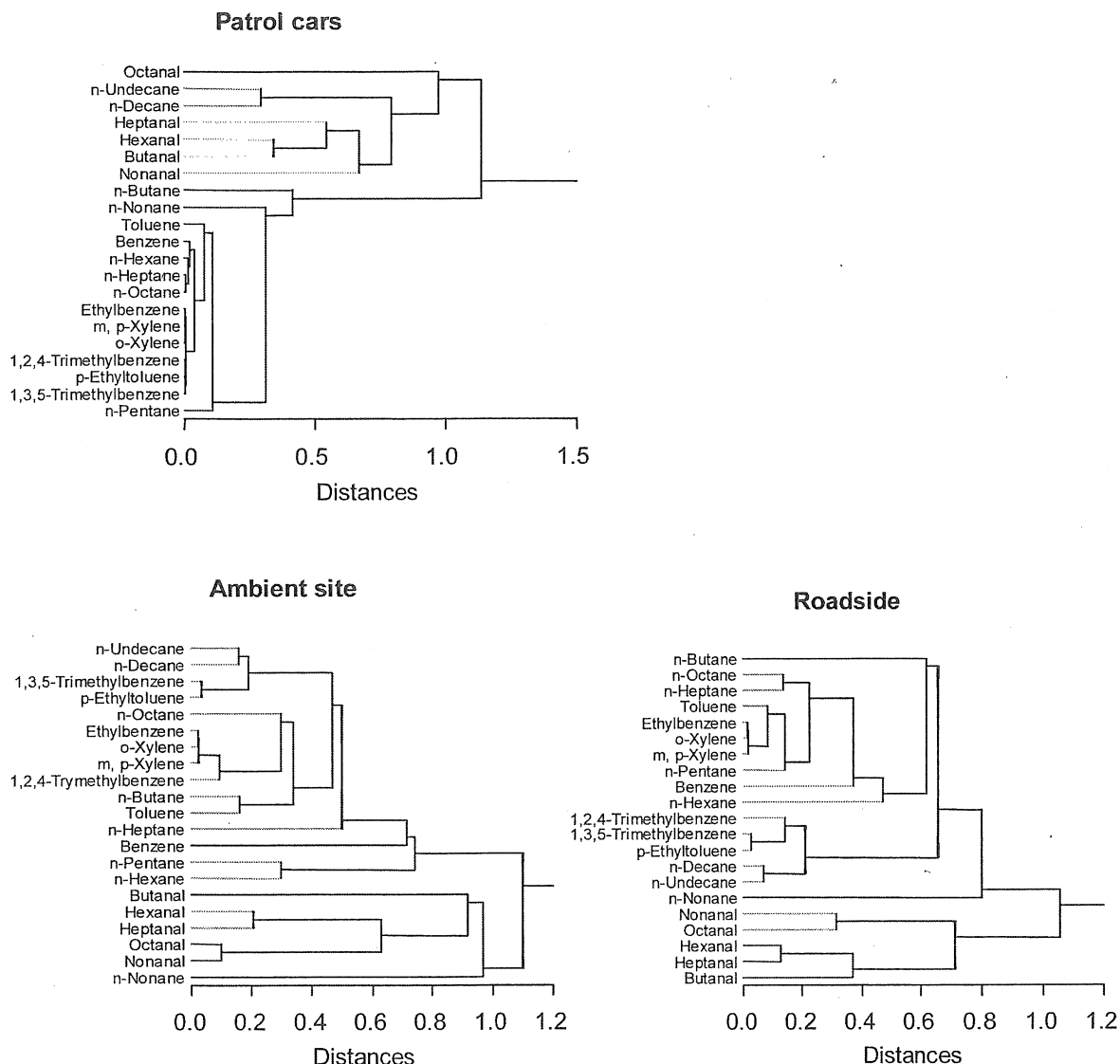


FIGURE 2. Cluster analysis of all VOC data collected with canisters. Clustering was calculated with the average distance method and the Pearson-distances.

locations (in nanograms per volume air). A comparison for the in-car sample composition with the ambient measurements is shown in Figure 3 (composition in nanograms per milligram sampled $PM_{2.5Mass}$). Sulfur is the dominant element and lies on the diagonal line indicating identical mass ratios at the two locations. Elements under this line are more concentrated in the $PM_{2.5}$ sampled inside the cars compared to the $PM_{2.5}$ mass collected at the ambient site. Significantly (Mann-Whitney U-test, $p < 0.05$) higher concentrated elements in the car samples are aluminum (Al), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), copper (Cu), strontium (Sr), and antimony (Sb). Significantly less concentrated elements are as follows: terbium (Tb), iridium (Ir), and mercury (Hg). A tendency (not significant, but $p < 0.1$) toward higher concentrations on samples from inside the cars was seen for phosphorus (P), lanthanum (La), and gold (Au), whereas samarium (Sm) and tantalum (Ta) tended to be lower inside the cars. The in-car concentrations of Sr had one extreme outlier of 26.3 ng/ μ g (excluded in Figure 3). This outlier was confirmed by a replicate XRF-measurement. The average $PM_{2.5}$ concentration of that shift was 7.5 μ g/ m^3 . The subsequent day the Sr-value in that car was still high (0.27 ng/ μ g) compared to the average (0.07 ng/ μ g without the outlier). The activity log

and the GPS recordings of the shift with the extreme Sr-level show that this was a patrol with little road activity, the trooper made one short stop at the police workshop, and the car was parked for about 6 h in downtown Raleigh near the legislative building with the trooper inside that building.

The elemental composition of the samples from the roadside locations was similar to the samples from the ambient site with the exception of higher roadside levels of particulate Ti (ambient: 0.24 ng/ μ g, roadside: 0.42 ng/ μ g, $p = 0.02$), Fe (3.18 vs 6.72 ng/ μ g, $p = 0.001$), Cu (0.11 vs 0.24 ng/ μ g, $p = 0.05$), and Sb (0.2 vs 0.41 ng/ μ g, $p = 0.03$). Sm was lower (0.0631 vs 0.0004 ng/ μ g, $p = 0.04$). None of the other elements showed a significant difference between the ambient site and the roadside locations.

Variability and Spatial Distribution of the Measurements. The within-shift variability of the in-vehicle measurements of speed, temperature, PAH, and CO was larger than the between-shift variability (Table 4). For the stationary sites, a similar difference between the two measures of variability occurred for carbon monoxide. The two stationary sites did not differ much with regard to the measures of variability. However, comparing the cars with both stationary sites shows a smaller between-shift variability for temperature and a larger within-shift variability for CO.

TABLE 3: Element Concentrations Inside the Vehicles and at the Two Stationary Sites^a

	patrol cars (P)				ambient site (A)				roadside (R)				Mann–Whitney-U-Test		
	mean	SD	min	max	mean	SD	min	max	mean	SD	min	max	P vs A	P vs R	A vs R
Na	276.8	65.4	131.4	434.4	324.8	90.9	159.0	508.7	329.6	78.4	189.3	514.5	0.031	0.006	0.983
Mg	6.1	9.4	0.0	32.1	7.9	11.9	0.0	52.1	7.8	10.4	0.0	40.8	0.353	0.494	0.878
Al	55.0	50.2	0.0	233.9	42.6	23.3	4.6	103.1	44.3	27.7	0.4	104.1	0.678	0.610	0.865
Si	198.2	464.3	28.9	3333.0	278.0	355.6	34.9	1778.8	337.7	672.0	43.9	3253.5	0.011	0.083	0.456
P	1.2	2.9	0.0	11.1	0.3	1.6	0.0	7.9	0.4	1.5	0.0	7.4	0.079	0.403	0.312
S	1592.4	905.2	249.0	3477.0	2225.3	1567.8	261.4	6149.0	2231.2	1415.7	287.0	5380.6	0.061	0.047	0.848
Cl	6.9	32.1	0.0	227.1	1.4	2.8	0.0	9.0	3.2	9.1	0.0	40.5	0.250	0.274	0.954
K	61.4	75.1	13.4	541.1	60.0	27.7	12.8	120.8	57.3	23.5	24.2	121.9	0.173	0.165	0.670
Ca	44.0	30.9	14.9	188.5	34.3	15.1	11.7	64.3	40.3	18.1	12.9	91.2	0.283	0.785	0.338
Sc	0.5	1.1	0.0	4.3	0.8	1.2	0.0	4.0	0.7	1.2	0.0	4.7	0.271	0.462	0.701
Ti	10.4	9.2	0.0	40.4	7.0	5.7	0.0	18.5	10.3	6.5	2.1	29.4	0.188	0.537	0.106
V	0.8	1.1	0.0	4.6	0.5	1.0	0.0	3.1	0.7	1.1	0.0	3.8	0.153	0.704	0.279
Cr	1.9	1.6	0.0	7.0	1.2	1.3	0.0	4.6	1.1	1.0	0.0	2.6	0.071	0.038	0.905
Mn	4.2	3.2	0.0	13.4	2.9	2.0	0.0	6.1	3.2	2.8	0.3	9.4	0.071	0.264	0.915
Fe	332.4	307.4	61.7	1426.8	86.0	46.1	26.3	208.4	162.5	82.2	59.0	420.8	<0.001	0.001	<0.001
Co	0.0	0.0	0.0	0.3	0.1	0.3	0.0	1.2	0.0	0.0	0.0	0.0	0.188	0.498	0.162
Ni	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.9	0.488	0.557	0.307
Cu	32.1	18.2	3.6	75.2	2.7	4.3	0.0	19.9	7.7	16.4	0.0	81.0	<0.001	<0.001	0.040
Zn	9.8	5.2	0.0	31.7	15.6	15.9	2.0	82.8	16.7	13.7	2.9	67.8	0.041	0.007	0.610
Ga	0.0	0.2	0.0	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.488	0.498	1.000
As	1.0	1.4	0.0	4.4	1.5	1.5	0.0	5.0	1.2	1.5	0.0	4.4	0.080	0.850	0.324
Se	1.2	1.2	0.0	4.0	1.6	1.5	0.0	4.0	1.6	1.2	0.0	4.2	0.370	0.126	0.931
Br	2.3	1.7	0.0	6.9	3.0	1.9	0.0	6.2	2.0	1.3	0.0	4.6	0.149	0.639	0.088
Rb	0.3	0.7	0.0	3.2	0.4	1.1	0.0	4.5	0.3	0.7	0.0	2.2	0.892	1.000	0.916
Sr	5.2	28.3	0.0	200.3	0.4	0.8	0.0	2.9	0.5	0.9	0.0	2.5	0.067	0.163	0.709
Y	0.5	0.8	0.0	3.1	0.6	0.8	0.0	2.7	0.8	1.4	0.0	4.3	0.207	0.372	0.801
Zr	2.0	2.7	0.0	11.9	1.8	2.5	0.0	8.0	1.8	2.0	0.0	6.8	0.912	0.679	0.538
Nb	1.5	2.1	0.0	7.2	2.1	3.0	0.0	10.4	2.2	2.7	0.0	10.3	0.475	0.247	0.765
Mo	1.5	2.5	0.0	10.0	2.3	3.1	0.0	10.7	1.8	2.3	0.0	8.0	0.170	0.234	0.850
Ag	6.2	6.8	0.0	30.0	4.8	6.6	0.0	21.7	3.1	4.5	0.0	15.9	0.304	0.087	0.676
Cd	3.7	5.7	0.0	24.9	3.5	4.1	0.0	12.4	3.7	6.8	0.0	26.0	0.820	0.502	0.460
In	4.4	6.6	0.0	23.7	4.4	7.4	0.0	33.0	2.0	4.5	0.0	20.6	0.985	0.090	0.126
Sn	14.7	12.1	0.0	46.0	14.8	11.6	0.0	38.7	16.4	11.0	0.0	39.6	0.830	0.487	0.602
Sb	10.9	14.2	0.0	82.4	4.8	8.1	0.0	27.2	9.1	9.2	0.0	28.9	0.028	0.942	0.041
Cs	11.3	16.5	0.0	66.7	12.8	19.5	0.0	61.1	22.3	25.6	0.0	74.8	0.685	0.055	0.177
Ba	95.5	46.4	0.0	189.0	99.4	44.3	16.8	210.8	98.2	28.3	40.2	154.2	0.760	0.695	0.798
La	28.3	36.3	0.0	141.3	16.0	23.1	0.0	71.6	21.7	32.6	0.0	132.4	0.134	0.342	0.556
Ce	36.3	44.7	0.0	194.0	50.1	52.1	0.0	176.4	25.4	38.4	0.0	143.8	0.356	0.298	0.099
Sm	0.5	2.0	0.0	13.2	1.5	3.3	0.0	10.8	0.0	0.1	0.0	0.3	0.086	0.383	0.039
Eu	0.4	1.1	0.0	4.3	1.4	3.1	0.0	10.4	0.2	0.6	0.0	2.6	0.240	0.983	0.363
Tb	0.0	0.0	0.0	0.0	0.3	1.2	0.0	6.0	0.0	0.0	0.0	0.0	0.040	1.000	0.162
Hf	1.9	3.5	0.0	16.3	1.7	2.4	0.0	6.3	2.2	2.6	0.0	7.4	0.856	0.256	0.424
Ta	1.2	2.9	0.0	15.5	2.5	3.5	0.0	12.8	2.6	3.5	0.0	9.9	0.033	0.012	0.775
W	6.3	5.8	0.0	19.5	4.9	4.9	0.0	16.7	4.5	5.9	0.0	19.7	0.437	0.114	0.359
Ir	4.6	4.7	0.0	13.5	10.8	4.8	0.0	21.9	8.3	5.4	0.0	17.5	<0.001	0.011	0.077
Au	3.8	3.6	0.0	16.8	3.0	3.4	0.0	10.1	4.0	3.9	0.0	11.2	0.253	0.853	0.278
Hg	1.1	1.6	0.0	5.3	2.9	3.3	0.0	9.5	3.8	2.7	0.0	9.8	0.012	<0.001	0.274
Pb	2.4	3.0	0.0	11.8	2.0	2.1	0.0	7.2	4.3	6.0	0.0	26.8	0.795	0.369	0.170

^a The concentrations are given in nanograms per cubic meter sampled air. This is in contrast to Figure 3, which shows weight ratios. The significance for difference was tested with the Mann–Whitney U-test. The *p*-values shown are for the comparison of the element concentrations per volume air, whereas the significances mentioned in Figure 3 and in the text compare the concentrations per sampled mass.

The spatial distribution of the PM_{2.5Realtime} measurements is shown in Figure 4 on a map of Wake County, NC. The graph shows the minute-by-minute concentrations of all recorded routes. The area of the circles is proportional to the concentration. The highest concentrations and most of the larger spots are associated with major roads, whereas the concentrations on residential and rural roads tend to be smaller.

The GPS recordings allowed clear identification of the location, direction, and speed of the trooper. The accuracy of the measurements differed depending on the topography: When the cars were parked on open roads and near flat buildings, consecutive position measurements differed by 0–10 m. However, when parked near tall buildings in downtown Raleigh, variations of up to 412 m were observed.

Discussion

During the study, air pollutant levels in Wake County were at moderate levels as reflected by the measurements at the ambient site and the roadsides. The official NCDENR monitors at Millbrook reported no exceedances of the NAAQS. Our PM_{2.5} monitors measured on average 30% higher mass concentrations than NCDENR's TEOM PM_{2.5} monitor. Our colocated samplers measured three values of PM_{2.5Realtime} and one of PM_{2.5Mass} during the 9-h measurement that would exceed the 24-h NAAQS for PM_{2.5} of 65 µg/m³. This difference is a well-known phenomenon due to heating losses of semivolatile components inside the TEOM (31, 32).

Inside the cars, all assessed pollutants were always well below current occupational standards. PM_{2.5} and ozone were lower inside the cars than at the ambient site and the roadside, whereas CO, elemental carbon, VOCs, and many metals were

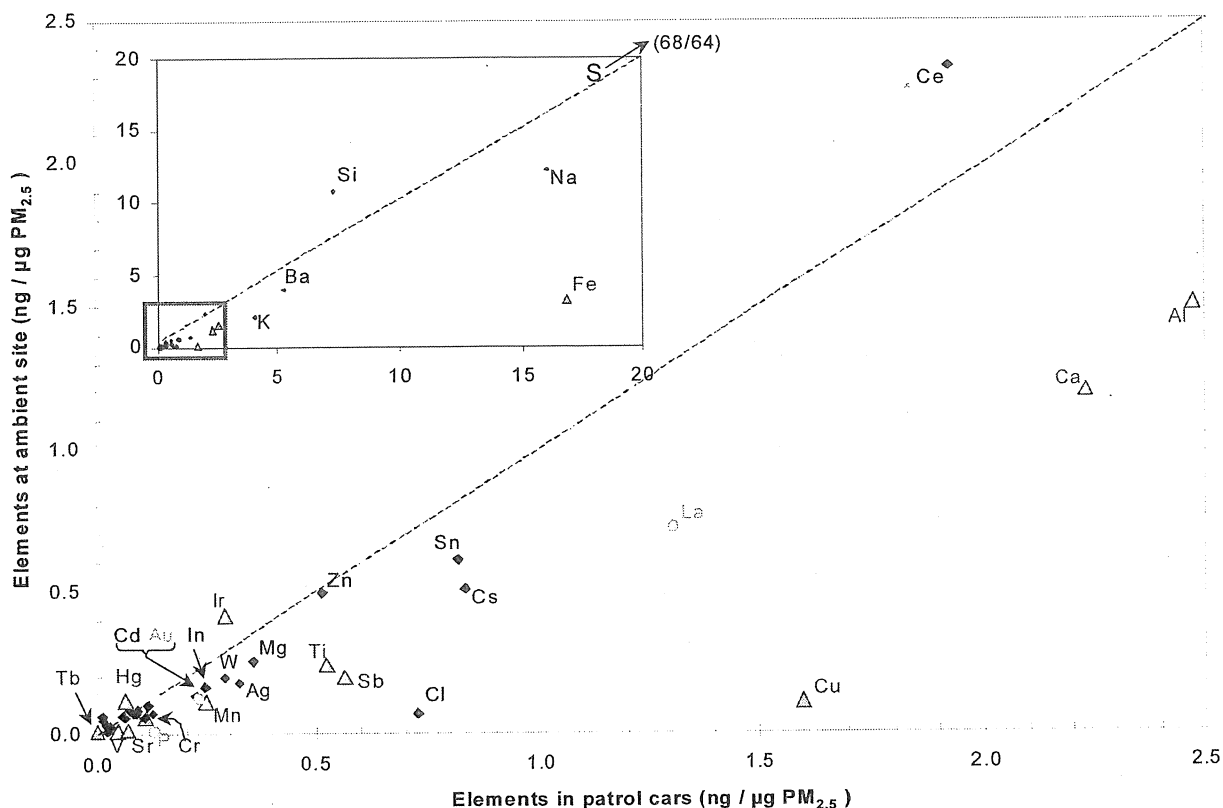


FIGURE 3. Element composition of the $PM_{2.5}$ fraction: comparison of the mean inside the patrol cars with the ambient site. The dashed line represents equal contribution to the total particle mass. Elements below the line are over represented in the car and vice versa. Significant differences (Mann–Whitney U-test, $p < 0.05$) are highlighted with red, near significances ($p < 0.1$) with green. Strontium (Sr) is shown without the extreme outlier (difference is significant with and without outlier). Sulfur was the abundant element (outside the range of the figure as indicated by an arrow and x/y -coordinates).

TABLE 4: Variability of the Continuously Measured Parameters^a

	mean	between shifts SD of daily averages	within shifts average daily SD
In-Vehicle Measurements			
speed	km/h	22.6	8.2 (36%)
temperature	°C	25.5	2.1 (8%)
relative humidity	%	35.8	5.5 (15%)
PAH	ng/m ³	21.5	10.3 (48%)
CO	ppm	2.6	1.1 (44%)
$PM_{2.5}Realtime$	μg/m ³	24.1	14.6 (61%)
Ambient Measurements			
temperature	°C	24.3	4.9 (20%)
relative humidity	%	62.9	13.7 (22%)
CO	ppm	0.8	0.3 (40%)
Roadside Measurements			
temperature	°C	23.3	4.8 (21%)
relative humidity	%	67.4	13.3 (20%)
CO	ppm	1.1	0.3 (31%)

^a Standard deviations as absolute values and as percentage of the mean-value.

higher. Gasoline engines emit CO, elemental carbon, and VOCs, which explains the elevated levels of these pollutants inside the cars. Ozone concentrations were only about one-third of the ambient levels. Ozone is known to have lower levels along streets due to its reaction with fresh exhaust gases such as nitric oxide (33).

However, $PM_{2.5}$ levels inside the cars were lower than at the ambient site, which is opposite to what was expected from a study in London (10), where $PM_{2.5}$ concentrations

inside automobiles were about doubled compared to urban background (33 vs 15 $\mu\text{g}/\text{m}^3$). It is also opposite to a study in California with several commuter-like road trips (34), where concentrations inside the cars were slightly higher than at ambient measurement sites (8.7 vs 10.2 $\mu\text{g}/\text{m}^3$ in Sacramento, 42.8 vs 43.8 $\mu\text{g}/\text{m}^3$ in Los Angeles), although $PM_{2.5}$ concentrations sampled outside at the base of the windshield were about 20% higher than inside the cabin. The cars in our study were not used during 35% of the shift. However, even when averaged over the times the trooper used the car, $PM_{2.5}$ remained slightly lower inside the cars compared to the ambient site. We explain the relatively low particle concentrations inside the patrol cars by the recirculation of air associated with the air conditioning unit, which was used by all troopers during most of the study period: first, the circulation reduced the amount of fresh air loaded with particles that entered into the cabin; second, the circulation supported the deposition of particles in the AC units and on other surfaces in the cabin. An earlier study on the fate of cigarette smoke inside vehicles showed that respirable particles had a greater decrease than the gaseous components of cigarette smoke (35). Their mass balance model suggested that this was due to deposition on surfaces inside the vehicle. We observed similar reductions in a particle exposure chamber of similar size as a car cabin when using a recirculation-type AC unit (data not shown).

The concentrations of VOCs inside the cars were much higher than the roadside and ambient measurements. The cluster analysis of the patrol car VOC species measurements (Figure 2) showed a tight link between the shorter n -alkanes (C_4 – C_9) and the monoaromatic compounds, which suggests the fingerprint of gasoline (36). Both findings point to cars

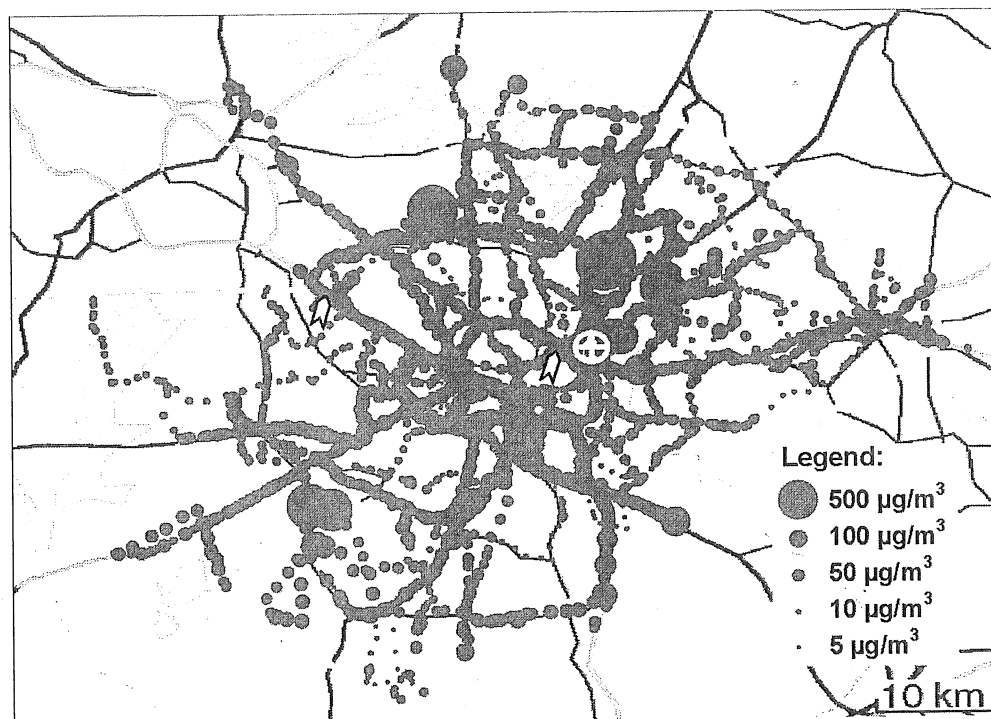


FIGURE 4. Spatial distribution of the $PM_{2.5}^{Realtime}$ measurements. The graph shows the minute-by-minute concentrations of all recorded routes on a map of Wake County, NC, in which the size of the circles represents the concentration level at that location. The ambient site for the urban background sampling is marked with a cross, the roadside locations with arrows.

as the source for the elevated levels of VOCs inside the vehicle. Our findings are in agreement with reports from Boston, where VOC concentrations inside cars were six to eight times elevated compared to ambient air (16). The question remains whether the patrol car itself or other cars are the source of the elevated VOC concentrations. A study conducted in 1988 in Raleigh reported VOCs to be up to six times higher in vehicles driven on roads with heavy traffic compared to low traffic (15), which favors other cars as the source. The troopers patrolled mostly on roads with heavy traffic, which is expected to lead to higher concentrations. An additional source of VOC could be that troopers refuel their cars on a daily basis. The gas station of the highway patrol is not equipped with a vapor recovery system for catching evaporated fuel, which is known to reduce the exposure to gasoline vapors during the fueling process by up to 99% (37). The contribution of this refueling is estimated to less than 10% of the total VOC exposure, if the exposure during a 10-minute refueling time is assumed to be at the average level of service station attendants (38). One patrol car had very high VOC concentrations that continued to increase from day to day. This might have been the consequence of a malfunctioning engine (39), though a routine service several weeks later found everything to work properly.

Although all the VOC concentrations were well below occupational thresholds, benzene is a known carcinogen for which exposure should be kept as low as possible. The average daily exposure of the troopers to benzene was in the range of the new European ambient standard of $5 \mu g/m^3$ ($= 1.6$ ppb) (40), if their exposure during the time off from work is assumed to be at ambient levels. Even though the European standard is set for the general population and does not constitute an occupational standard, reductions in the occupational benzene exposure of the troopers would be desirable.

NO_2 concentrations inside the cars were always low. Only one high concentration was observed (548.5 ppb, 8-h TLV: 1000 ppb), which we cannot explain since no other pollutant was elevated during that shift.

Sulfur was the most common element in the XRF analysis. Figure 3 shows that sulfur is present in the same mass-proportion in $PM_{2.5}$ inside the cars as in the ambient air. Sulfur in fine particles originates from combusting fossil fuels such as coal and diesel (41). These combustion processes also contribute importantly to the total mass of $PM_{2.5}$. Particles inside the patrol cars seemed to be of ambient origin (as witnessed by the high sulfur association) but enriched by gasoline combustion-related species. Several elements are far below the line of identity: Cu and P were about 15 times higher in the cars compared to ambient $PM_{2.5}$. Fe, V, and Sr were about four times higher, while Al, Ca, Ti, Cr, Mn, Sb, Au, and La were about two times higher. Brake abrasion is the likely source for Cu (42) and P (P is an impurity in Cu from the ore mineral copper phosphate hydroxide). Chrome vanadium steel is used in cars for moving parts such as axles, shafts, transmission, and other components, which constitutes a source for Fe, V, and Cr. In oil refineries, zeolites are used as catalysts to crack hydrocarbons, which yields fractions with higher octane numbers (43). These zeolites contain cations such as K, Ca, Ba, and La in their pores that leach out during the cracking processes. Mn, Ti, V, and Al are natural components of petroleum and iron originates in the form of process-accumulated rust (44). These trace components of gasoline were similarly increased inside the cars, which points to the combustion of gasoline as the likely source. The reason for the increased level of strontium during one shift remains unclear.

Sm on airborne dust was found at very high concentrations at the ambient site. These levels were within the range observed at a heavily coal-smoke polluted site in Beijing, China (45). Sm was increased only at the ambient site but not at the roadside and not significantly inside the cars. Sm is used commercially in products such as magnets and lasers. It is likely that the increased ambient Sm levels reflect some (unidentified) local industrial source.

The within-shift variability in the cars was for all variables much larger than the between-shift variability (Table 3). This result suggests that the variability of the concentrations was

driven primarily by the variety of daily duties of the troopers rather than by differences between days or between troopers. Being inside a moving vehicle may be the most important factor. The largest variabilities were in PAH and CO rather than PM_{2.5}. If both PAH and CO were related to vehicular exhausts, it suggests that driving in heavy traffic causes large swings in those gasoline-burning markers. The CO-levels inside automobiles were previously found to be related to the surrounding traffic density (46), and roadside CO measures also show larger within-shift than between-shift variance, which both support this idea.

The map of Wake county in Figure 4 shows the spatial distribution of PM_{2.5}Realtime concentrations. Several hot spots with very high concentrations are apparent. At first sight, there does not seem to be a large difference between rural (yellow background) and urban areas (grey). Instead, concentrations appear to be higher on main roads compared to side roads, independent of the land use surrounding the roads. Matching the data obtained in this study to a dynamic air pollution model of Wake County, which includes local topography and small scale wind flow models, might help to assess the impact of the time and location of a car on the concentration inside the vehicle.

The accuracy of the GPS differed in different topographical settings. Tall buildings introduced a large error into the location measurements when the cars were parked. However we had few problems with the moving patrol cars, probably because Wake County is relatively flat and has only few tall buildings (mainly clustered in central Raleigh), which can interfere with the timed signals from the GPS-satellites.

These observational data document levels of particulate and gaseous air toxics in highway patrol cars in a suburban area of the southern United States during the warm and humid fall season. Air pollutant levels were consistently below current occupational threshold limits. PM_{2.5} levels in cars were lower than the ambient and roadside levels, a finding probably attributable to the use of recirculation air conditioners in the cars with deposition of particles on the surfaces inside the vehicle. CO, aldehyde, and VOC levels were several times higher in the cars than at the ambient location and roadside locations, and roadside CO levels were higher than ambient levels. The comparison of levels of pollutants with geographic location suggests that concentration of traffic is a critical element in determining in-cabin levels. These findings suggest that technical means of reducing and excluding pollutants from the engine into the cabin are effective, while emissions from other cars contribute largely to the exposure inside the vehicle. The investigated patrol cars were modern and well maintained, while older cars might have an additional exposure to pollutants from the own engine. The concentrations reported here therefore probably reflect the lower end of what can be expected inside vehicles in an urban center such as Raleigh. Furthermore, the positive association with traffic volume around this relatively small urban center raises many questions about the future health effects from carbon fuel-burning vehicles for the people living near centers that grow in population and traffic density.

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